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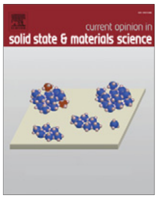

The pursuit of rechargeable non-aqueous lithium–oxygen battery cathodes

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ABSTRACT

To satisfy the energy storage needs of society in the long-term, an advance in battery energy density is required. The lithium–oxygen battery is one of the emerging opportunities available for enhanced energy storage. The challenge for the Li–O_2 battery is the progress of development of the O_2-cathode that allows reversible formation of Li_2O_2 in a stable electrolyte within its pores.

1. Introduction

A breakthrough in energy density is required to satisfy the energy storage needs of society in the long-term. Lithium–air batteries (hereafter referred to as lithium–O_2 batteries since O_2 is the reactant) have theoretical specific energies almost 10 times that of the state-of-the-art Li-ion battery technology (Table 1). For practical energy densities these values reduce to factor of 2–3 improvement, which would still provide a major step change in energy storage capability [1]. Certainly if the lithium metal anode would operate successfully in a Li–O_2 cell, then the positive energy storage benefit for the Li metal/$LiCoO_2$ cell would also be realised (Table 1). Until recently non-aqueous Li–O_2 cells have been in the background of battery science, but since the demonstration of the working principle of a rechargeable Li–O_2 cell by Abraham and Jiang [2], and then multiple cycling of a lithium–O_2 cell by Bruce and co-workers [3], there has been a "gold rush" by research groups around the world to develop this emerging system for energy storage applications [4–10]. In this fast moving field there have already been a number of reviews on all aspects of the Li–O_2 cell [1,11–17]. However, the unique and crucial aspect of the Li–O_2 cell is the reaction (or reactions) at the O_2-cathode. It is this topic which the present review addresses. Within the limited space available, we cannot hope to review all the excellent work that has taken place on Li–O_2; instead we will focus solely on recent developments of the O_2 cathode for Li–O_2. The review starts with an overview of the non-aqueous Li–O_2 cell followed by sections on the role of the electrolyte, the potential role of catalysts and finally on optimisation of porosities and creating novel electrode architectures for air cathodes to increase the power capability of Li–O_2.

2. The non-aqueous Li–O_2 cell

Unlike a conventional battery where the reagents are contained within the cell, the Li–O_2 cell uses oxygen from the atmosphere. The Li–O_2 cell can be thought of as a battery–fuel cell hybrid, although it is more a derivative of metal–air batteries (e.g. Zn–air). A schematic representation of the rechargeable non-aqueous Li–O_2 cell is shown in Fig 1. On discharge, lithium ions formed at the lithium metal anode are transported across the electrolyte and into the pores of the O_2-cathode. O_2 from the atmosphere enters the cathode, and dissolves into the electrolyte within the pores. It is then reduced at the porous carbon electrode surface by electrons from the external circuit and combines with Li^+ from the electrolyte, leading to the formation of solid Li_2O_2 as the final discharge product. Somewhat surprisingly, the reaction is reversible, Li_2O_2 can be oxidised, releasing oxygen gas, thus making this an energy storage device, $2Li + O_2 \leftrightarrow Li_2O_2$ [3].

The large increase in theoretical specific energy on migrating from Li-ion to Li–O_2 arises because Li_2O_2 in the cathode can store more Li, and hence more charge, than $LiCoO_2$ per unit mass and Li metal stores more charge per unit mass than graphite (C_6Li). Some authors have reported that discharge to Li_2O is possible [4,6,19], which would further enhance the potential for stored energy (Table 1). However, the oxidation of Li_2O may require even greater overpotentials during charge, unless suitable catalysts can be employed [20].

3. Mechanism of ORR and OER in non-aqueous Li–O_2 cells

Studies of O_2 reduction in non-aqueous electrolytes have been carried out for several decades, but very few addressed the conditions found in Li–O_2 cells [21–26]. In this respect, if progress is to be made on Li–O_2 batteries, it is important to understand the

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Table 1
Data for several electrochemical reactions that form the basis of energy storage devices.

Battery	Cell voltage (V)	Theoretical specific energy (W h kg^{-1})	Theoretical energy density (W h L^{-1})
Today's Li-ion	3.8	387	1015
½C_6Li + $Li_{0.5}CoO_2$ = 3C + $LiCoO_2$			
Li metal/$LiCoO_2$	3.9	534	2755^a
½Li + $Li_{0.5}CoO_2$ = $LiCoO_2$			
Li–O_2 (non-aqueous)			
2Li + O_2 = Li_2O_2	3.0	3505	3436^b (Li + Li_2O_2)
4Li + O_2 = Li_2O	2.91	5220	3819^c (Li + Li_2O)

[a] Density of $LiCoO_2$ = 5.16 kg L^{-1} [18].
[b] Based on the sum of the volumes of Li at the beginning and Li_2O_2 at the end of discharge.
[c] Based on the sum of the volumes of Li at the beginning and Li_2O at the end of discharge.

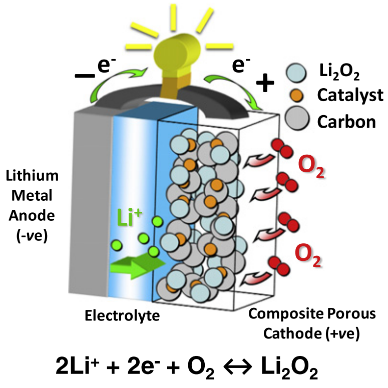

Fig. 1. The non-aqueous lithium–oxygen cell.

fundamental mechanism of O_2 reduction in the presence of Li^+ and the formation of Li_2O_2, as well as the mechanism of Li_2O_2 oxidation on charging. Recent detailed electrochemical investigations have probed the influence of salt and solvent on the O_2 reduction reaction (ORR) [4,9,27]. *In situ* Raman microscopy and mass spectrometry have also been applied [3,28], which offer the important benefit of identifying directly the species involved in the reactions (intermediates and products) on discharge and charge.

The current consensus from the various studies is that the mechanism of O_2 reduction on discharge is:

$$O_2 + e^- \rightarrow O_2^- \tag{1a}$$
$$O_2^- + Li^+ \rightarrow LiO_2 \tag{1b}$$
$$2LiO_2 \rightarrow Li_2O_2 + O_2 \tag{1c}$$

However, other studies suggest the occurrence of direct reductions [4,9]:

$$LiO_2 + Li^+ + e^- \rightarrow Li_2O_2 \tag{1d}$$
$$Li_2O_2 + Li^+ + e^- \rightarrow 2Li_2O \tag{1e}$$

Reaction (1d) occurs at lower voltages than 1(a) [28] and there has to date been incomplete evidence for the formation of Li_2O.

For the oxygen evolution reaction (OER) gas analysis from charging of Li_2O_2 shows that the oxidation of Li_2O_2 follows:

$$Li_2O_2 \rightarrow 2Li^+ + 2e^- + O_2 \tag{2}$$

The reaction course on charging is not the reverse of discharge; the latter involves O_2^- as an intermediate, whereas from the evidence provided from the experiments so far performed, the former does not. The strongest confirmation is from the utilisation of propylene carbonate (PC) as the electrolyte [3,28]. As discussed in further detail later, PC is unstable in the presence of O_2^- leading to by-products including CO_2 [29]. Because of the absence CO_2 detected during the charging of Li_2O_2 in PC, it can be inferred that no O_2^- is generated during the charging process. Furthermore *in situ* Raman (Fig. 2), shows no signal pertaining to O_2^- or LiO_2 during the charging of Li_2O_2 on Au [28].

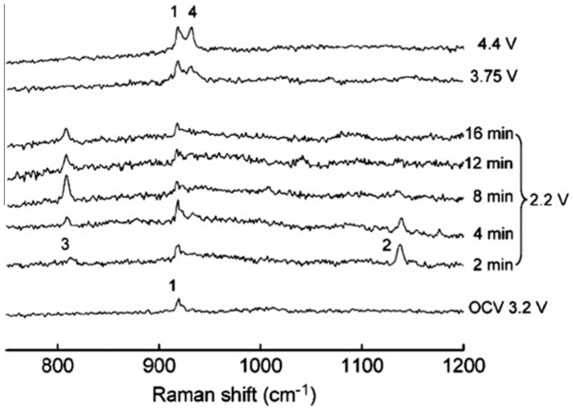

Fig. 2. *In situ* SERS during O_2 reduction and re-oxidation on Au in O_2-saturated 0.1 M $LiClO_4$–CH_3CN. Spectra collected at a series of times and at the reducing potential of 2.2 V vs. Li/Li$^+$ followed by other spectra at the oxidation potentials shown. The peaks are assigned as follows: (1) C–C stretch of CH_3CN at 918 cm^{-1}, (2) O–O stretch of LiO_2 at 1137 cm^{-1}, (3) O–O stretch of Li_2O_2 at 808 cm^{-1}, (4) Cl–O stretch of ClO_4^- at 931 cm^{-1}. Figure reproduced with permission from Ref. [28], © 2011 Wiley.

4. Challenges for the O_2-cathode

The challenges for the O_2 cathode are shown in Fig. 3. A typical O_2-cathode is comprised of a carbon black mixed with a polymeric binder. The porous carbon O_2-cathode is required to ensure a large electrolyte/electrode surface area and accommodate the insoluble discharge product (Li_2O_2), as well as to facilitate oxygen diffusion to the reaction site through the cathode film. In addition, the porous carbon network must provide enough conductivity to deliver electrons to the reaction site efficiently with low overall impedance. A homogenous distribution of a nano-sized catalyst may also be required to maximise the performance by increasing the round-trip efficiency by lowering the voltage gap between charge and discharge processes; however this has been challenged recently as discussed below. For practical Li–O_2 cells an exterior O_2 permeable membrane is required to prevent the ingress of water and carbon dioxide, whilst still allowing the free passage of oxygen. Progress on membrane development is reported in recent reviews [1,17]. Alternatively the Li–O_2 cell could be used without a membrane if O_2 gas is obtained from an air stream scrubbed of H_2O and CO_2. Such engineering solutions would lead to the lowering of possible energy storage of the final system.

5. The electrolyte

The electrolyte is currently the biggest obstacle to progress in Li–O_2 cells. Understanding, controlling and hence eliminating side reactions is a significant undertaking. The electrolyte must be stable to O_2 and its reduced species, as well as the Li_xO_y compounds that form on discharge; it must exhibit sufficient Li^+ conductivity, O_2 solubility and diffusion to ensure satisfactory rate capability, as well as wet the electrode surface and possess low volatility to avoid evaporation at the cathode.

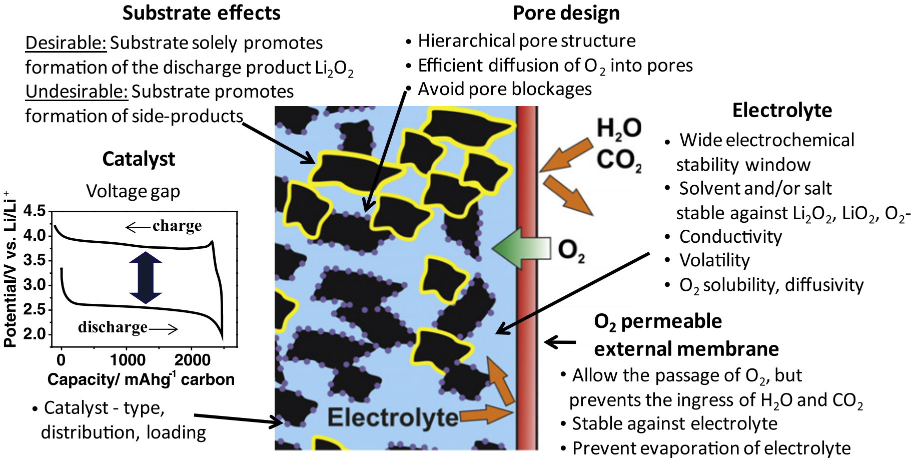

Fig. 3. Challenges facing the O_2-cathode of the lithium–oxygen cell.

5.1. Organic carbonates

Early Li–O_2 cells employed an organic carbonate-based electrolyte, either PC or a blend of cyclic and linear carbonates e.g. ethylene carbonate:dimethylcarbonate. Typical lithium salts were lithium hexafluorophosphate ($LiPF_6$) or lithium bis(trifluoromethylsulfonyl)imide (LiTSFI). Organic carbonate-based electrolytes were chosen because of their low volatility, compatibility with Li metal and high oxidation stability (>4.5 V vs. Li/Li^+), and a lower toxicity when compared to other organic solvents.

Aurbach et al. [30] indicated organic carbonate instability in the presence of O_2 in the early 1990s when studying the effects of contaminants (O_2, H_2O) on the performance of Li-ion batteries. Nevertheless, many groups reported multiple cycling of Li–O_2 cells [2,3,7,31]. It was assumed that the ability to cycle such cells implied reversible formation of Li_2O_2 while the capacity fading was due to side reactions with the electrolyte.

In 2010 Mizuna et al. [10] and Bruce and co-workers [32] independently reported data which demonstrated that instability in organic carbonate was a much more important issue. Mizuna showed infrared data that revealed the presence of $RCOO_2Li$ and Li_2CO_3 in discharged cells, whilst Bruce and co-workers presented data that showed the gas released on recharge of a discharged cell was predominantly CO_2 (98% CO_2 vs. 2% O_2) [32] (see Fig. 4). Significantly, these studies revealed that there is little or no evidence of Li_2O_2 formation occurring in parallel with the electrolyte degradation. Further data soon emerged from IBM [8], PNNL [33,34] and ORNL [35] that supported these early studies and ruled out the remarkable ability of Li–O_2 cells with organic carbonate electrolytes to sustain cycling (up to 100 cycles) to be due to reversible Li_2O_2 formation. Instead, the cycling of Li–O_2 cells in organic carbonate occurs by degradation of the electrolyte on discharge to form lithium propyl dicarbonate ($C_3H_6(OCO_2Li)_2$), Li_2CO_3, HCO_2Li, CH_3CO_2Li, CO_2 and H_2O, with these decomposition products being oxidised on charge, i.e. by repeated cycles of irreversible degradation and *not* reversible Li_2O_2 formation [29]. The implication of these findings is that rechargeable Li–O_2 cells containing organic carbonate electrolytes will not work. For a rechargeable battery truly reversible reactions must occur at the electrodes.

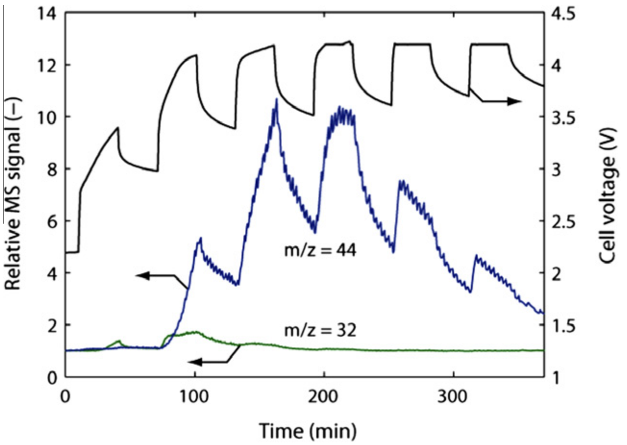

Fig. 4. Differential electrochemical mass spectroscopy (DEMS) of Li–O_2 cell on charging after discharge in 1 M $LiPF_6$, PC. CO_2 (*m*/*z* = 44) is the dominant gas evolved (98%) on charging, along with to a small signal (2%) associated with O_2 evolution (*m*/*z* = 32) is present [32].

5.2. Ethers

Attention switched recently to the study of ethers, most notably tetraglyme, ($CH_3O(CH_2CH_2O)_4CH_3$) [27,36], triglyme ($CH_3O(CH_2CH_2O)_3CH_3$) [37] and dimethoxyethane (DME, $CH_3OCH_2CH_2OCH_3$) [8,27,38,39]. Such ethers are more stable than organic carbonates towards reduced O_2 and do exhibit Li_2O_2 formation at ~2.7 V, at least on the first discharge. Investigation of linear (diglyme, triglyme and tetraglyme) and cyclic (1,3 dioxolane, 2-methyl tetrahydrofuran) ethers in Li–O_2 cells established that electrolyte degradation does take place leading to the formation of Li_2CO_3 and HCO_2Li, and CH_3CO_2Li [40]. Studies of DME in Li–O_2 cells by mass spectrometry showed that only ~60% of the O_2 consumed on discharge is released on charge [8]. Oligoether-functionalised silane based electrolytes have recently been reported to show a greater stability to oxygen reduction products and no Li_2CO_3 was observed in the FTIR of discharged electrodes [41]. Though ethers are more stable than carbonate electrolytes, they are not yet the final solution to the challenge of identifying a suitable non-aqueous electrolyte for Li–O_2 batteries that allows multiple cycling with little to no fading [8,40]. As shown by powder XRD (Fig. 5), Li_2O_2 is present on the 1st discharge but is absent on the 5th cycle discharge.

5.3. Ionic liquids

Hydrophobic ionic liquids have properties that are favourable for practical Li–O_2 cells as they are non-flammable, non-volatile, and, due to their hydrophobic properties, will better protect the metal anode from moisture in comparison to other aprotic

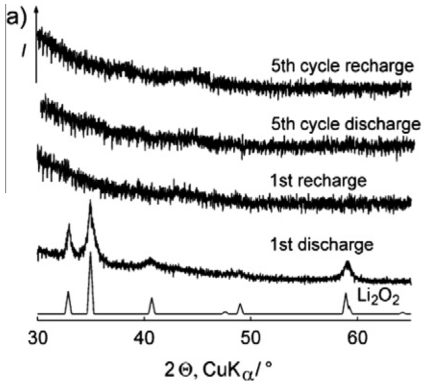

Fig. 5. Powder X-ray diffraction patterns of the composite cathode (Super P/Kynar) cycled in 1 M $LiPF_6$ in tetraglyme under 1 atm O_2 between 2 and 4.6 V vs. Li/Li$^+$. Figure reproduced with permission from Ref. [40], © 2011 Wiley.

solvents. However, O_2 solubility and diffusivity are likely to be lower in this class of electrolytes, which is likely to impact on the power output of such cells. Superoxide formation has been demonstrated in several ionic liquids using cyclic voltammetry without the presence of a metal salt [42–45]. In the context of the Li–O_2 cell, two recently published papers show the effect of a lithium salt on the voltammogram. Both papers show that the presence of Li$^+$ leads to superoxide instability with the formation of insoluble lithium–oxygen species that passivate the glassy carbon working electrode. In addition Allen et al. [46] reported that, conversely a gold electrode demonstrated more efficient recharging, with multiple cycling without passivation, providing evidence that the role of the substrate requires much greater understanding. The investigation of hydrophobic ionic liquids in a primary Li–O_2 cell established that they can maintain less than 1% H_2O content after 100 h of operation, in the case of 1-ethyl-3-methyl imidizolium bis (trifluoromethane sulfonyl)imide. On discharge, a capacity of 5360 A h kg^{-1} (based on carbon alone) has been demonstrated for operation of up to 56 days [47]. Mizuna et al. [48] have shown that a Li–O_2 cell can be cycled in an ionic liquid however the capacities so far reported are lower at around 200 A h kg^{-1}(total electrode mass). As in the case of other electrolyte studies, it will be important in future work on ionic liquids to determination the nature of the discharge products with spectroscopic methods, in order to identify any side-reactions due to electrolyte decomposition.

5.4. Solid electrolytes

The first report of the rechargeable non-aqueous Li–O_2 cell by Abraham and Jiang [2] used a polymer based electrolyte in the form of a polymeric gel with a typical blend comprising of 12 w/o polyacrylonitrile (PAN)–40 w/o ethylene carbonate (EC)–40 w/o propylene carbonate (PC)–8 w/o $LiPF_6$. Three discharge/charge cycles of 100 A h kg^{-1} (carbon) were reported. Other solid electrolytes in the form of both ceramics and polymers have been investigated subsequently, in particular cells incorporating the lithium ion conductor: lithium aluminium germanium phosphate (LAGP, $18.5Li_2O{:}6.07Al_2O_3{:}37.05GeO_2{:}37.05P_2O_5$). Cells were shown to maintain 40 cycles at elevated (40–100 °C) temperatures [49]. Moreover the use of nitrogen doped carbon in this configuration was shown to improve capacities [50]. Other ceramics such as the LISICON type glass ceramic (LIthium SuperIonic CONductor, $Li_{(1+x+y)}Al_xTi_{2-x}Si_yP_{(3-y)}O_{12}$ marketed by Ohara Inc., Japan), have been employed, which show large voltage gaps of 2.5 V, with at least 15 cycles and little fading of ca. 500 A h kg^{-1}(carbon) [51]. In addition, Li–O_2 cells consisting of a solid polyethylene oxide based electrolyte could be charged at the relatively low voltage of 3.6 V [9]. Studies of Li–O_2 cells with solid electrolytes have provided some attractive results and solid electrolytes may prove more stable towards superoxide than liquid electrolytes. However, as for the ionic liquids, work is required to identify the all the discharge products, before concluding whether or not Li_2O_2 is formed in significant amounts. All solid electrolyte Li–O_2 cells (Fig. 6a), will suffer from the problem of operating with a three component boundary (Fig. 6b), where the number of locations where O_2 gas, electrons and lithium ions can meet are limited This is compounded by the formation of a solid (Li_2O_2) discharge product at these sites, something that is not a problem in fuel cells where the discharge products is volatile (H_2O). Specific cell architectures may help (Fig. 6c and d), but the core problem of a three component boundary and the creation of a solid product remains.

5.5. Lithium salt

Much attention has been devoted to the stability or instability of the solvent; fewer studies exist on understanding the role of the lithium salt. XPS data [52] have shown that $LiPF_6$ exposure to Li_2O_2 causes the formation of a thick layer of LiF on the Li_2O_2. $LiPF_6$ decomposition has also been observed by XPS on MnO_2/C O_2-cathodes from discharged Li–O_2 cells [35]. This is deleterious to the Li–O_2 cell both from the loss of lithium and electrolyte salt in the formation of inactive decomposition products, but also from the potential detrimental effect on the oxidation of Li_2O_2 by the modification of the interface between Li_2O_2 and the O_2-cathode surface. Decomposition products of lithium bis(oxalate)borate (LiBOB) have also been reported, both by chemical reaction with Li_2O_2 [52] or LiO_2 [53]. $LiClO_4$ been shown to be more stable against Li_2O_2 [52], but may suffer from lower oxidative stability whilst LiTFSI and lithium bis(fluorosulfonyl)imide (LiFSI) have been proposed as more stable salts for use in the Li–O_2 cell [53].

5.6. Electrolyte additives

One method of improving the performance of Li–O_2 cells is to use additives that increase the solubility of Li_2O_2 in the electrolyte. This could increase the oxidation kinetics and hence charging rate. Additives that increase the O_2 solubility could increase the discharge rate. Enhancing the power capability of Li–O_2 cells is an important target. Organo-boron Lewis acids such as tris(pentafluorophenyl) borane (TPFPB) $B(C_6F_5)_3$ have been reported to increase of the dissolution of Li_2O_2 in carbonate-based organic solvents [54]. Boron esters have also been investigated [55] and the presence of diol-monoacid-borate was shown to increase the solubility of Li_2O_2 in EC:DMC by an order of magnitude from 0.29 to 3.2 mmol L^{-1}. Tetrabutyl ammonium cation (TBA$^+$) has also been proposed to aid in the dissolution of oxygen reduction products [4]. To increase the solubility of O_2 in electrolytes a small amount (0.5%) of perfluorotributylamine was added to 1 M $LiPF_6$ in PC [56]. A factor of 5 increase in the peak current for O_2 reduction was recorded. This general research direction looks promising and will need to be repeated in more stable electrolytes, in order to observe and understand the effect of these perfluorinated additives in Li–O_2 cells. Nevertheless, if Li_2O_2 solubility becomes too great, then significant amounts will ultimately migrate as solubilised peroxide to the lithium anode. Insulating films of lithium oxides would then result on the lithium surface, which would detrimental to the functioning of the device by increasing resistivity of the anode interface.

5.7. Binder

In terms of finding stable components for Li–O_2 cells, such as solvent and salt, it should be mentioned that very recent work by Black

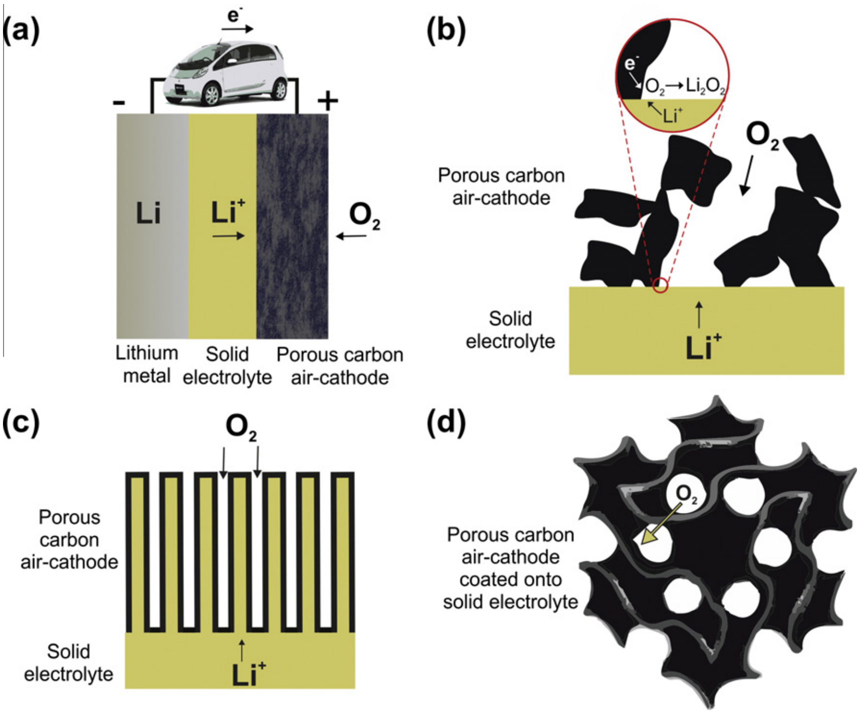

Fig. 6. (a) Schematic of a solid electrolyte Li–O_2 cell, (b) issues of three component boundary, to improve three component boundaries employ either (c) rod architecture, or (d) porous network.

et al. [57] have shown that stable binders are also required. They found that superoxide actively dehydrofluorinates polyvinylidene difluoride (PvDF, also known as Kynar-Flex), which is the most commonly utilised binder in O_2^- cathodes. The resultant by-products react further with the transition metal–oxide catalyst, such as α-MnO_2, to produce LiOH which accumulates at the interface, as detected by FTIR and XRD in Li–O_2 studies in ether-based electrolytes [40,57]. Lithiated Nafion has been found to be relatively unreactive with respect to superoxide and therefore may be a preferred future choice for a more stable binder in future Li–O_2 studies [5,57].

5.8. Future electrolytes

The search for an electrolyte that is stable towards reduced oxygen species and Li_2O_2, thus permits highly reversible Li_2O_2 formation/decomposition remains one of the major challenges for the rechargeable Li–O_2 battery. Note that it is not enough to simply demonstrate reversible formation of surface layers of Li_2O_2. Although this is useful for mechanistic studies [4,28], it is necessary to show that highly reversible Li_2O_2 formation/decomposition with a relatively high capacity is possible, if the non-aqueous rechargeable Li–O_2 battery is ever to be possible. Computational methods of screening solvent susceptibility of nucleophilic attack by superoxide have been undertaken and are likely to improve our understanding of suitable candidate electrolytes [58]. Experimentally it is important to use techniques such as FTIR and differential electrochemical mass spectrometry to identify and quantify side reactions and reversibility.

6. The O_2-cathode

6.1. Substrate effects

The role of the substrate (in most cases carbon) and the catalyst, included to reduce the voltage gap by promoting oxidation of Li_2O_2, will become an increasing focus of attention, especially once more stable electrolytes are identified. In particular, understanding how the substrate affects the reaction mechanism, the degree of side reactions and reversibility of Li_2O_2 formation/decomposition will be crucial areas for study.

Experiments so far have revealed little mechanistic understanding of the role of carbon in the O_2-cathode. Preliminary modelling studies [59] conclude that carbons with a high concentration of oxygen surface groups promote oxygen reduction. McCloskey et al. [8] found that although electrolyte decomposition was the major source of CO_2 during cell charging, cathode carbon oxidation contributed about 4% of total CO_2 production. Whether the oxidation occurred from carbon surface functional groups directly, or from carbon surface functional groups that had reacted with superoxide to form surface decomposition products, remains to be identified. Furthermore, whether oxygen functional groups on the carbon surface are regenerated by exposure of oxygen reduction products during discharge is another avenue of prospective research in understanding the role of the substrate. Certainly research efforts should be made to ascertain if carbon is an intrinsically suitable conductive substrate for Li–O_2. Indeed, as mentioned previously, it has been observed that gold is a more reversible substrate than glassy carbon in cyclic voltammetry studies in ionic liquids [46]. Both electrolyte and substrate are important factors to understand and control in the Li–O_2 battery.

6.2. Catalysts for Li–O_2

The requirement for a catalyst in the Li–O_2 cell is still unclear. Many early studies were carried out in electrolytes containing organic carbonates [3,5,7,19,60,61], which decompose on discharge [10,29]. As a consequence, the catalyst therefore is catalysing the electrolyte decomposition on discharge and the oxidation of the decomposition products on charge [29]. Future studies will have to be repeated in more stable electrolytes, which at least for the first discharge–charge cycle exhibit significant formation and decomposition of Li_2O_2. For the OER the effect of various catalysts

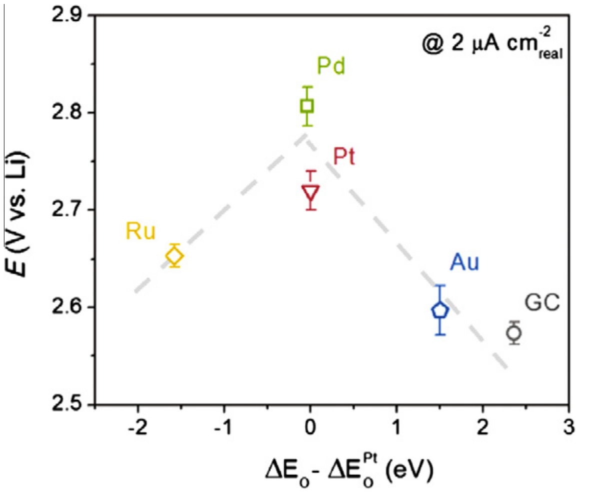

Fig. 7. Volcano dependence on O_2 adsorption energy vs. ORR activity. Figure reproduced with permission from Ref. [64], © 2011 ACS.

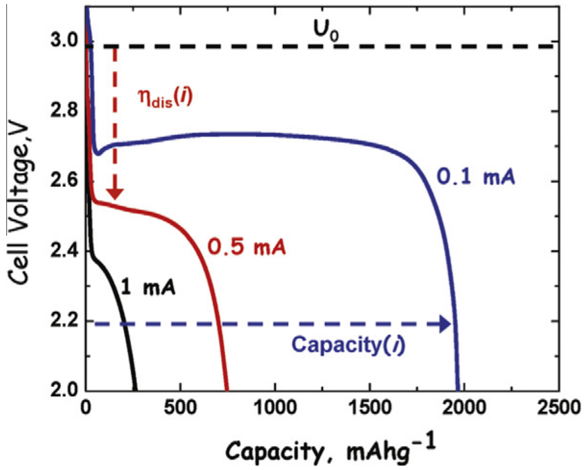

Fig. 8. Discharge curves for a Li–O_2 cell (based on a carbon black O_2-cathode) Figure reproduced with permission from Ref. [11], © 2011 ACS.

on the electrochemical oxidation of Li_2O_2 ($Li_2O_2(s) \rightarrow 2Li + O_2\uparrow$) have been investigated by charging electrodes constructed with Li_2O_2 included within the as-prepared cathode [62]. PC based electrolyte was employed but this is stable on oxidation so does allow examination of Li_2O_2 oxidation. The study included a variety of transition metal oxides, with nanowires of α-MnO_2 giving the lowest charging voltage in Li–O_2 cells of 3.5 V vs. Li/Li$^+$. Overall, it was demonstrated that catalysts do indeed lower the charging voltage plateau of Li_2O_2 [62].

Conversely IBM [63] recently reported that an OER catalyst is not required due to the observation that oxygen is primarily evolved at low depths of discharge at a potential of 2.9 V, which is only just above the open circuit potential of the discharged cell (2.8 V). Additional work is therefore required to see if O_2 evolution also occurs at low potentials in O_2-cathodes preloaded with Li_2O_2, which will avoid any side-reaction complications from discharge. For the ORR it has been shown that the inclusion of MnO_2 [40] or Pt [63] increase the proportion of electrolyte decomposition in the more stable ether-based electrolytes. The major mechanism leading to increased electrolyte decomposition results from breakdown products, generated by the reaction of superoxide with PVdF binder, reacting with catalysts in the O_2-cathode to form LiOH, as was discussed earlier in the review [57] Lu et al. [64] demonstrated that O_2 adsorption energy on the surface can greatly influence Li$^+$-ORR activities and that a volcano dependence can be inferred (Fig. 7). Activities were shown to be in the order of Pd > Pt > Ru ≈ Au > GC. Accompanying work comparing the performance of noble metals with transition metal oxides would be attractive.

6.3. Structure

As shown by Fig. 8. increasing the discharge current drastically reduces the capacity in Li–O_2 cells, indicating the problem with kinetics [11]. This has motivated many authors to examine novel O_2-cathode architectures, in order to increase power capability. In aqueous systems gas diffusion electrodes are employed in which the gas is carried in hydrophobic channels then dissolves in the electrolyte within hydrophilic channels that are in very close proximity. In this way the O_2 is transported mainly in the gas phase, rather than the much slower diffusion in the liquid. Of course such architecture is harder to engineer with non-aqueous electrolytes. Assuming a suitable gas diffusion electrode that ensures facile O_2 transport can be constructed, and then a high electrode surface area is necessary. However high surface areas imply small pores that could become blocked by solid Li_2O_2, so a compromise is necessary between high active surface area and adequate pore size, the compromise is expected to be found in the mesoporous region. Additionally, the optimisation of the relative amounts of carbon, catalyst and binder, and their distribution will be important.

Growing carbon nanofibre carpets onto a porous ceramic substrate produced not only high specific energies of up to 2500 W h kg^{-1} (based on electrode mass), but also specific power up to 1000 W kg^{-1} at a specific energy of 1000 W h kg^{-1} [38]. Co_3O_4 nanorods grown onto nickel foams have been shown to deliver good performance (up to 4000 A h kg^{-1} total electrode mass) and low voltage gaps (0.5 V at a low current density of 0.02 mA cm^{-2}), but without sustained cycling [65]. Another design solution involved using hierarchical porous graphene [37], where its structure permitted access of O_2 to most of the graphene sheets. Extremely large capacities were reported of up to 15,000 A h kg^{-1} (based on mass of carbon). On the other hand, increasing the amount of binder with respect to carbon was found to substantially reduce capacities because of pore blockage [66]. Once again when more stable electrolytes are available the ability of these novel structures to sustain many cycles of significant formation and oxidation of Li_2O_2, will be able to be better understood.

7. Summary

The non-aqueous rechargeable Li–O_2 cell holds significant promise for high energy storage applications, but it is a long way from being a technological product. Fundamental challenges in all aspects of the cell, anode, electrolyte and cathode, need to be addressed. The reaction at the cathode (reversible formation of Li_2O_2) is what defines the non-aqueous Li–O_2 cell and represents one of the major current challenges; therefore we have concentrated on this in the present review. Recent studies have shown that finding an electrolyte/electrode combination that permits highly reversible formation/decomposition of Li_2O_2 on sustained cycling (i.e. formation of high purity Li_2O_2 with minimal side reaction on discharge and then its complete oxidation on charge), is a key problem. Rechargeable batteries need to be based on truly reversible reactions and the ability to cycle a cell is not proof of true reversibility. This highlights the importance of using analytical techniques such as FTIR and DEMS, in order to demonstrate the purity for Li_2O_2 formation and its complete oxidation on charge. Major gaps in fundamental knowledge of the Li–O_2 cell remain, for example the true role of the catalyst. As a result, much ground-breaking and exciting science remains to be done.

One fact is certain, society requires energy storage devices with much higher levels of energy storage than ever before. Non-aqueous Li–O_2 cells are amongst the few contenders that can exceed the stored energy of Li-ion therefore continuing research efforts are essential in order to solve the scientific challenges of the Li–O_2 cell.

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